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UNITED STATES ATOMIC ENERGY COMMISSION

THE RECOVERY OF URANIUM FROM
COMMERCIAL 30% PHOSPHORIC ACID WITH
ANTIMONY

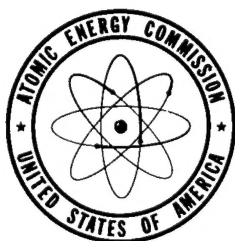
Summary Status Report

By
R. H. Bailes

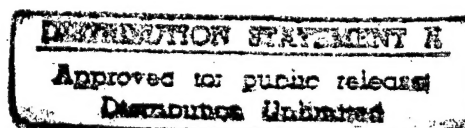
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February 23, 1950

Great Western Division
Dow Chemical Company
Pittsburg, California



Technical Information Extension, Oak Ridge, Tennessee



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SUMMARY STATUS REPORT

THE RECOVERY OF URANIUM FROM COMMERCIAL
30% PHOSPHORIC ACID WITH ANTIMONY

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R. H. Bailes

February 23, 1950

Great Western Division
THE DOW CHEMICAL COMPANY
Pittsburg, California

Contract No. AT-30-1-GEN-236

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A. SUMMARY

A preliminary estimate of the cost of recovering one pound of U_3O_8 , in the form of a solid assaying 12% U_3O_8 , from commercial 30% H_3PO_4 by means of Sb_2O_3 is \$13.28. A plant costing \$496,000 would be required in order to process 500 tons of 30% H_3PO_4 per day. As an alternative procedure, 3.2% of the 30% H_3PO_4 output can be diverted to $NH_4H_2PO_4$ manufacture. One pound of U_3O_8 in the same concentration plus 126 pounds of fertilizer-grade $NH_4H_2PO_4$ could then be produced for an estimated \$14.31 from a plant costing \$513,000. If a credit of \$0.05 per pound of $NH_4H_2PO_4$ produced can be accepted, the cost of U_3O_8 by this process would be reduced to about \$8.00 per pound. Ninety percent of the uranium in the phosphoric acid is recovered in either process.

Both of these estimated production costs are based on a plant producing 500 tons of 30% H_3PO_4 per day with a U_3O_8 assay of 0.00818 percent. Both include the sulfuric acid required to manufacture the phosphoric acid removed from the plant stream, but do not include costs of stepping up phosphoric acid production. In the first case production must be increased by 2.8 percent; in the second, by 3.2 percent.

In both processes the phosphoric acid is reduced with iron and is then agitated for a time with a small amount of antimony trioxide. The resulting solid is filtered off and is treated with dilute ammonia. When the ammonia is filtered, the filtrate contains 87% of the uranium originally in the phosphoric acid, and the residual solid consists of antimony trioxide, which is recycled. The phosphoric acid is returned to the plant.

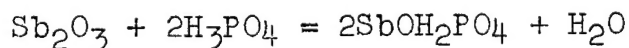
Ammonia is stripped from the ammonia filtrate in a special plate column in the first process, and the resulting liquor is filtered, yielding the 12% U_3O_8 product. The filtrate is treated with lime and the dicalcium phosphate thus produced is collected and delivered to the phosphoric acid plant for conversion to phosphoric acid. The filtrate, which contains ammonia, is combined with the ammonia distillate from the plate column and recycled.

In the second process three-fourths of the ammonia filtrate is evaporated in a triple effect evaporator. The dilute ammonia boiled out is condensed and recycled. The thickened liquor if filtered, yielding the 12% U_3O_8 product. The filtrate from the 12% U_3O_8 product is mixed with phosphoric acid, refiltered to recover antimony thus precipitated, evaporated, and dried to recover 126 pounds of monobasic ammonium phosphate per pound of U_3O_8 recovered.

B. INTRODUCTION

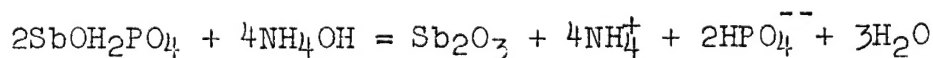
Commercial 30% H_3PO_4 contains small quantities of iron and vanadium which are present in such states that the oxidation state of about half of the uranium present is +6. In order to coprecipitate uranium from the acid with Sb_2O_3 , it is necessary to have essentially all the uranium in the +4 oxidation state. Scrap iron provides the most economical means of accomplishing this. Two grams of iron are consumed per liter of 30% H_3PO_4 , and the oxidation potential of the acid is thus increased from -0.3 to 0.0 volt, as measured by the platinum-saturated calomel electrode couple.

Antimony trioxide reacts slowly with phosphoric acid according to the following reaction:



No heat effects have been observed during the reaction. Uranium is coprecipitated along with the antimonyl di-hydrogen phosphate as uranous phosphate. Small portions of other cations are also coprecipitated. When 12.5 grams of powdered Sb_2O_3 are agitated with one liter of 30% H_3PO_4 (specific gravity = 1.21) which has been reduced as specified, 91 percent of the uranium is found in the SbOH_2PO_4 thus produced. This applies to a three-hour agitation period. From H_3PO_4 containing 0.10 gm. U_3O_8 per liter a precipitate is obtained which assays about 0.5% U_3O_8 .

The precipitate is converted to Sb_2O_3 by dilute ammonia solutions, according to the reaction:



The reaction is rapid and exothermic. If 100 percent excess 1 M ammonia is used, 95 percent of the uranium dissolves as a phosphate complex. The final pH of the system is about 9.5. About two percent of the antimony dissolves, presumably also as a phosphate complex.

When ammonia is boiled out of the solution a precipitate is obtained which assays 12% U_3O_8 (dry basis). Its properties resemble those of AlPO_4 , and in addition to aluminum it contains quantities of Sb, V, Cr, Fe, Ca, Al, Mg, and Ti. The only anion of importance is phosphate. The resulting solution has a pH of 6.5. Of the uranium present in the original ammoniacal solution, 96 percent reports in the precipitate. The mechanism seems to consist of a decrease in solubility of the uranous phosphate complex as the species of phosphate changes from 100 percent HPO_4^{--} to 84

percent H_2PO_4^- and 16 percent HPO_4^{--} . Coprecipitation with the AlPO_4 is also apparently involved.

Disposition can be made of the solution remaining after the 12% U_3O_8 is filtered off in two ways; lime treatment to remove phosphate, or addition of H_3PO_4 and evaporation to produce fertilizer-grade $\text{NH}_4\text{H}_2\text{PO}_4$. If the latter is chosen, about two-thirds of the antimony which dissolved in the ammonia can be recovered as SbOH_2PO_4 after addition of the phosphoric acid.

C. PROCESS FLOW

The flow sheet for the two processes considered in this report is presented in Figures 1, 2, and 3. The first parts of the two processes are the same, and the flow sheet corresponding to them is given in Figure 1. The flow sheet for the first process, which produces CaHPO_4 for return of phosphate to the plant, is completed in Figure 2. Figure 3 describes the last part of the second process, which produces $\text{NH}_4\text{H}_2\text{PO}_4$.

Antimony Trioxide Precipitation

Commercial 30% H_3PO_4 flows through a column containing scrap iron and is introduced into the Sb_2O_3 mixer, a 100-gallon vessel with provision for vigorous agitation. Vigorous agitation is necessary to prevent the Sb_2O_3 , introduced in the make-up as a powder, from clumping and coating with SbOH_2PO_4 , which would prevent further reaction. The thin slurry is led into three agitated 6000-gallon tanks arranged in series to provide an effective three-hour reaction period.

The slurry of 30% H_3PO_4 and SbOH_2PO_4 is filtered, and the SbOH_2PO_4 is washed and introduced into the NH_3 treatment vessel, which has a residence time of one hour. The H_3PO_4 , which has dissolved 0.12 gram Sb per liter, is returned to the plant with 91 percent of its uranium and 2.8 percent of its phosphate removed.

1.72 percent NH_3 solution in 100 percent excess is introduced into the NH_3 treatment vessel and the resulting slurry is filtered in the NH_3 filter. The solid from the filter is Sb_2O_3 , which is recycled. The filtrate, designated ammonia filtrate, is the source for uranium recovery by either of the two processes under consideration.

First Process - CaHPO_4 Production

Twenty percent ammonia is stripped from the ammonia filtrate in a distillation unit consisting of a heat exchanger, distillation column, reboiler, and condenser. The distillation column must be of such design that solid particles which form during the distillation will not be trapped on the plates. Cooling water is assumed available at 75° F. with a 30 degree rise.

To the 20% NH_3 condensate is added sufficient anhydrous ammonia to make up for any lost ammonia and the mixture is dissolved in the 0.53% NH_3 from the CaHPO_4 filter. The resulting solution is cooled and recycled to the NH_3 treatment vessel.

The bottoms from the distillation unit are filtered to recover the 12% U_3O_8 product, and the filtrate is mixed with lime in the lime tank. $CaHPO_4$ is filtered off and delivered to the H_3PO_4 plant for treatment with H_2SO_4 . The resulting H_3PO_4 will contain nearly all the uranium originally in the $CaHPO_4$.

Second Process - $NH_4H_2PO_4$ Production

The ammonia filtrate is preheated and evaporated to one-fourth volume. The vapors are condensed to recovery ammonia, mixed with make-up ammonia and water, and cooled to produce the dilute ammonia solution required in the NH_3 treatment vessel. Standard vertical tube evaporators are specified because of the precipitation taking place during evaporation.

The thick liquor is filtered to obtain the 12% U_3O_8 product. Phosphoric acid is added to the filtrate, the result being a precipitate of mixed phosphates, which is filtered off and returned to the NH_3 treatment vessel. Thus, two additional pounds of U_3O_8 per day appear in the ammonia filtrate and consequently in the 12% U_3O_8 product.

After the $SbOH_2PO_4$ is filtered off, the solution is evaporated to produce 126 pounds of $NH_4H_2PO_4$ per pound of U_3O_8 produced.

D. DISCUSSION

The first process, which returns phosphate to the phosphoric acid plant in the form of CaHPO_4 , requires a plant investment of \$496,000 and produces a solid assaying 12% U_3O_8 at a cost of \$13.28 per pound U_3O_8 . Tables I, II, and III detail the costs. The phosphate removal from the 30% H_3PO_4 amounts to 2.8 percent, and cost of the H_2SO_4 required to compensate for this removal is included in the estimate.

The second process, which manufactures $\text{NH}_4\text{H}_2\text{PO}_4$ instead of returning phosphate to the phosphoric acid plant, requires a plant costing \$513,000 and produces a solid assaying 12% U_3O_8 at a cost of \$14.31 per pound U_3O_8 . 126 pounds $\text{NH}_4\text{H}_2\text{PO}_4$ are produced per pound U_3O_8 . Table II itemizes the cost corresponding to the 3.2 percent phosphate removal.

No allowance was made in either estimate for the phosphate rock required to supply the phosphate. In the first process, this would amount to 0.2 percent, since phosphate is actually returned to the plant. In the second process, 3.2 percent of the phosphate rock costs are chargeable, but have been neglected. No charge was made for sizing or packaging the $\text{NH}_4\text{H}_2\text{PO}_4$, since it was assumed that it would be used by the H_3PO_4 plant.

Because of the value of the antimony, no thickener was specified before filtration of the H_3PO_4 . The slurry settles rapidly, but it leaves a colloidal suspension, which is slow to clarify, above the solid. The cost of a thickener of sufficient area to allow this suspension to clarify would be prohibitive.

The first process has one disadvantage. In order to distill out the ammonia from the ammonia filtrate, it is necessary to use a column designed to avoid clogging by the particles of 12% U_3O_8 product precipitated simultaneously, and plate efficiency would have to be sacrificed. This column and associated equipment must also be cleaned out regularly.

Substantial economies could be effected in both processes if either or both the settling and filtration characteristics of SbOH_2PO_4 were improved. If further research shows that the same uranium recoveries are obtainable from more concentrated ammonia treatments (the amount of NH_3 being the same), reductions in distillation equipment evaporator investment and steam consumption could be secured.

However, these processes require a rather large number of pieces of equipment to recover a very small amount of uranium, 12 tons per year, so there is a limit to the savings possible without change of process or increase in throughput. This limit is probably no greater than two dollars per pound U_3O_8 .

E. APPENDIX

TABLE I

ESTIMATED COST OF PLANT TO RECOVER URANIUM
FROM COMMERCIAL 30% H_3PO_4 BY MEANS OF ANTIMONY TRIOXIDE

Basis: 500 T 30% H_3PO_4 per day.

<u>Source of Cost</u>	<u>$CaHPO_4$ Production</u>	<u>$NH_4H_2PO_4$ Production</u>
Installed Process Equipment	\$157,000	\$165,000
Process Piping	47,000	50,000
Instrumentation	16,000	17,000
Manufacturing Buildings	47,000	50,000
Auxiliary Facilities	8,000	8,000
Outside Lines	8,000	8,000
Engineering and Construction	85,000	86,000
Contingency	85,000	86,000
Size Factor	43,000	43,000
Total	\$496,000	\$513,000

TABLE II

ESTIMATED COST OF RAW MATERIALS TO RECOVER URANIUM FROM
COMMERCIAL 30% H₃PO₄ BY MEANS OF ANTIMONY TRIOXIDE

Basis: 500 T 30% H₃PO₄ per day. Assay of 0.00818 weight percent U₃O₈. Ninety percent stream efficiency.
 Recoveries indicated on figures.

<u>Raw Material</u>	<u>Cost per ton</u>	<u>Cost per lb. U₃O₈ Produced</u>	
		<u>CaHPO₄ Production</u>	<u>NH₄H₂PO₄ Production</u>
Scrap Iron	\$ 20	\$0.23	\$0.23
Sb ₂ O ₃	540	1.24	.77
NH ₃	75	.07	.72
CaO	9	.24	.00
H ₂ SO ₄	10	.65	.84
		<u>\$2.43</u>	<u>\$2.56</u>

TABLE III

ESTIMATED COST OF PRODUCTION OF A SOLID ASSAYING 12% U_3O_8
FROM COMMERCIAL 30% H_3PO_4 BY MEANS OF ANTIMONY TRIOXIDE

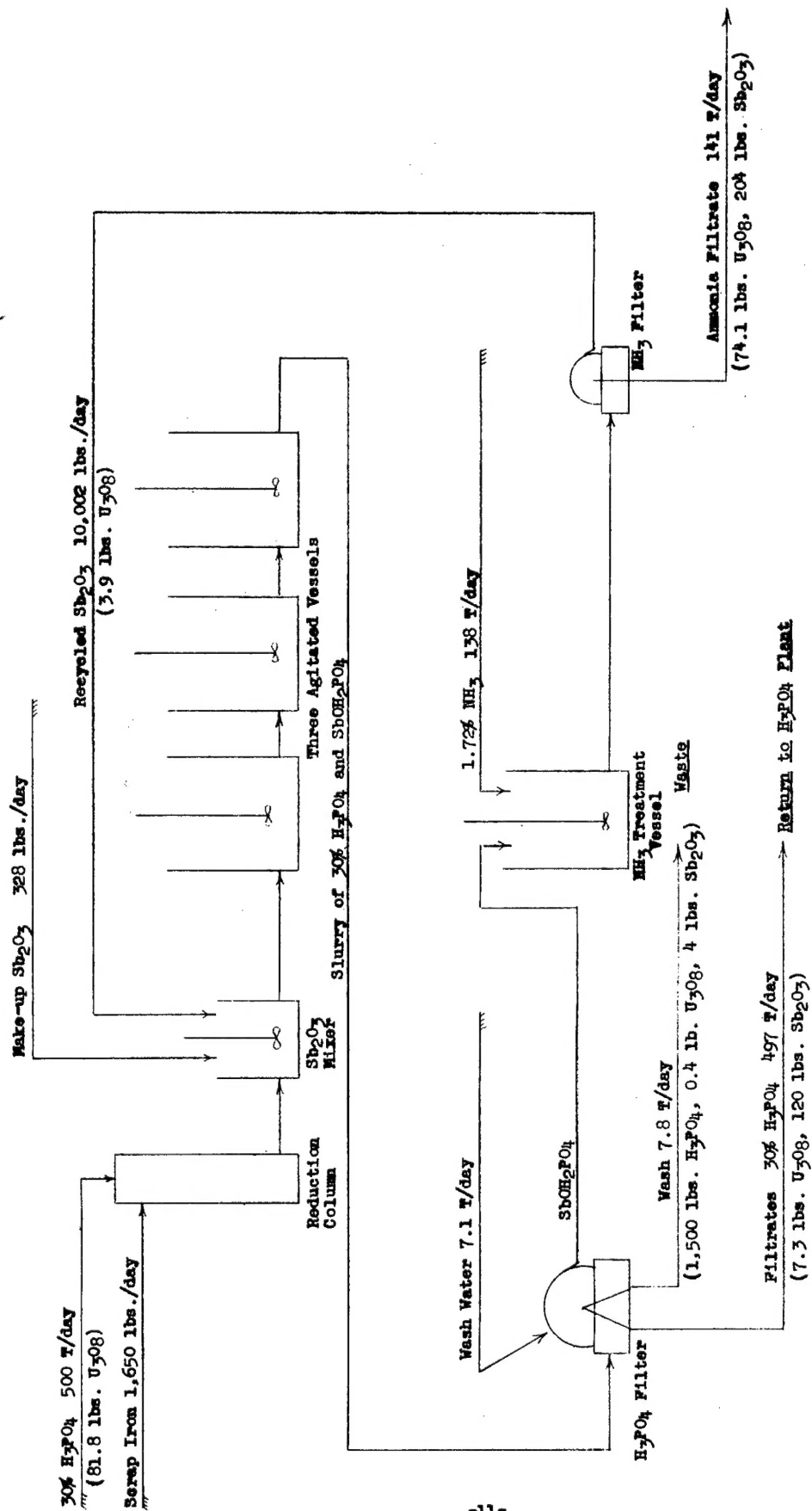
Basis: 500 T 30% H_3PO_4 per day. Assay of 0.00818 weight percent U_3O_8 . Ninety percent stream efficiency.
 Production as indicated on figures.

<u>Source of Cost</u>	<u>Basis</u>	<u>Cost per lb. U_3O_8 Produced</u>	
		<u>C_2HPO_4</u> <u>Production</u>	<u>$NH_4H_2PO_4$</u> <u>Production</u>
Operating Labor	Note (1)	\$ 1.94	\$ 1.89
Supplies	\$10 per man-mo.	.05	.05
Utilities: Steam	\$1/T	.37	1.08
Electricity	1.2¢/kwh.	.37	.37
Water	5¢/M gal.	.12	.30
Fuel	\$2.40/bbl.	.00	.05
Maintenance Labor	5% investment/yr.	1.06	1.07
Maintenance Material	5% investment/yr.	1.06	1.07
Laboratory	Note (2)	0.17	0.17
Insurance and Taxes	2% investment/yr.	0.42	0.43
Factory Expense	100% of labor	3.17	3.13
Depreciation	10% investment/yr.	2.12	2.14
Total Processing Cost		\$ 10.85	\$ 11.75
Raw Materials		2.43	2.56
Total Production Cost		\$ 13.28	\$ 14.31*

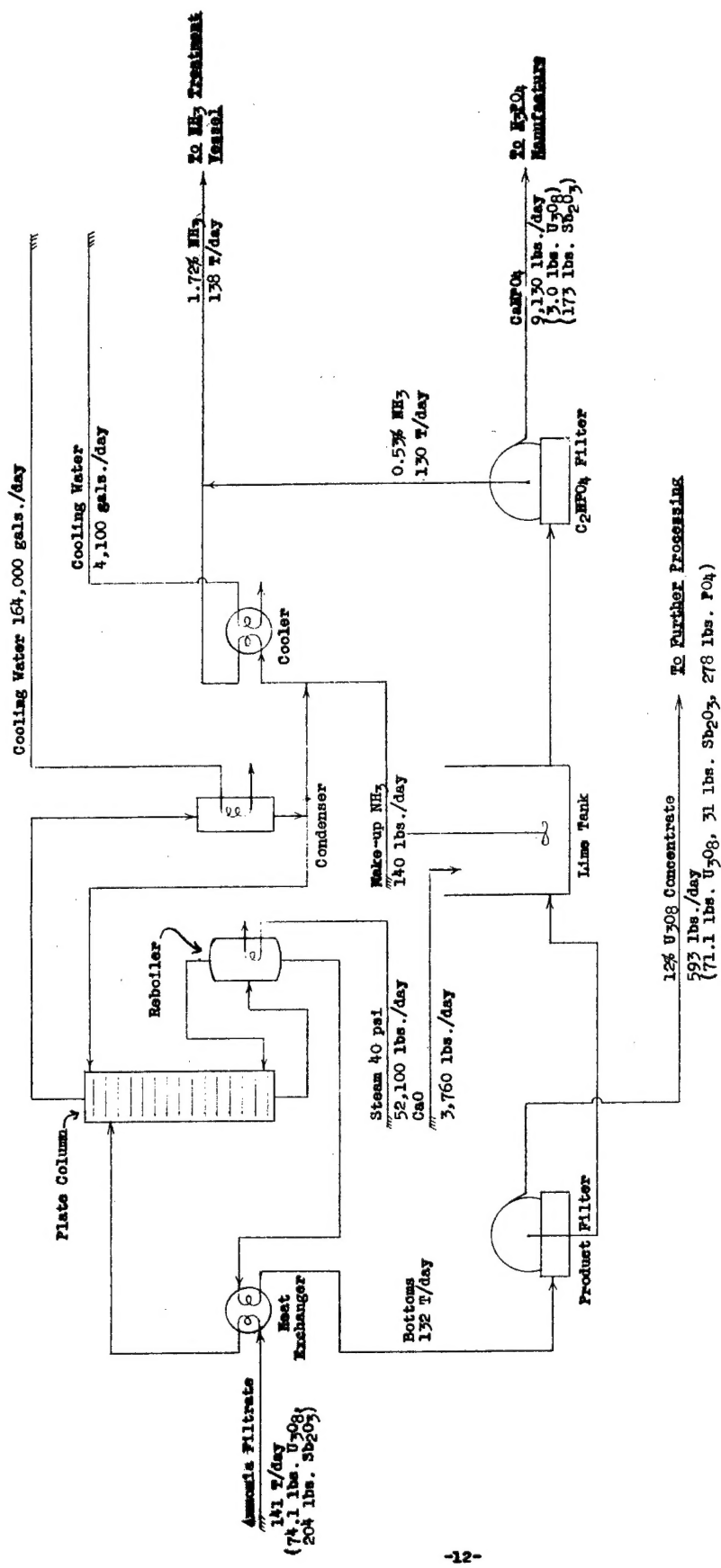
*Less credit for 126 lbs. $NH_4H_2PO_4$

Notes: (1) 3 operators 24 hours per day at \$1.50 per hour
 plus one supervisor at \$6000 per year.

(2) Chemist at \$4000 per year.



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Figure 1.		
Antimony Fluoride Precipitation Plant Sketch		
DRAWN	DATE	SCALE
De Haeze	Jan 19 50	
TRACED		



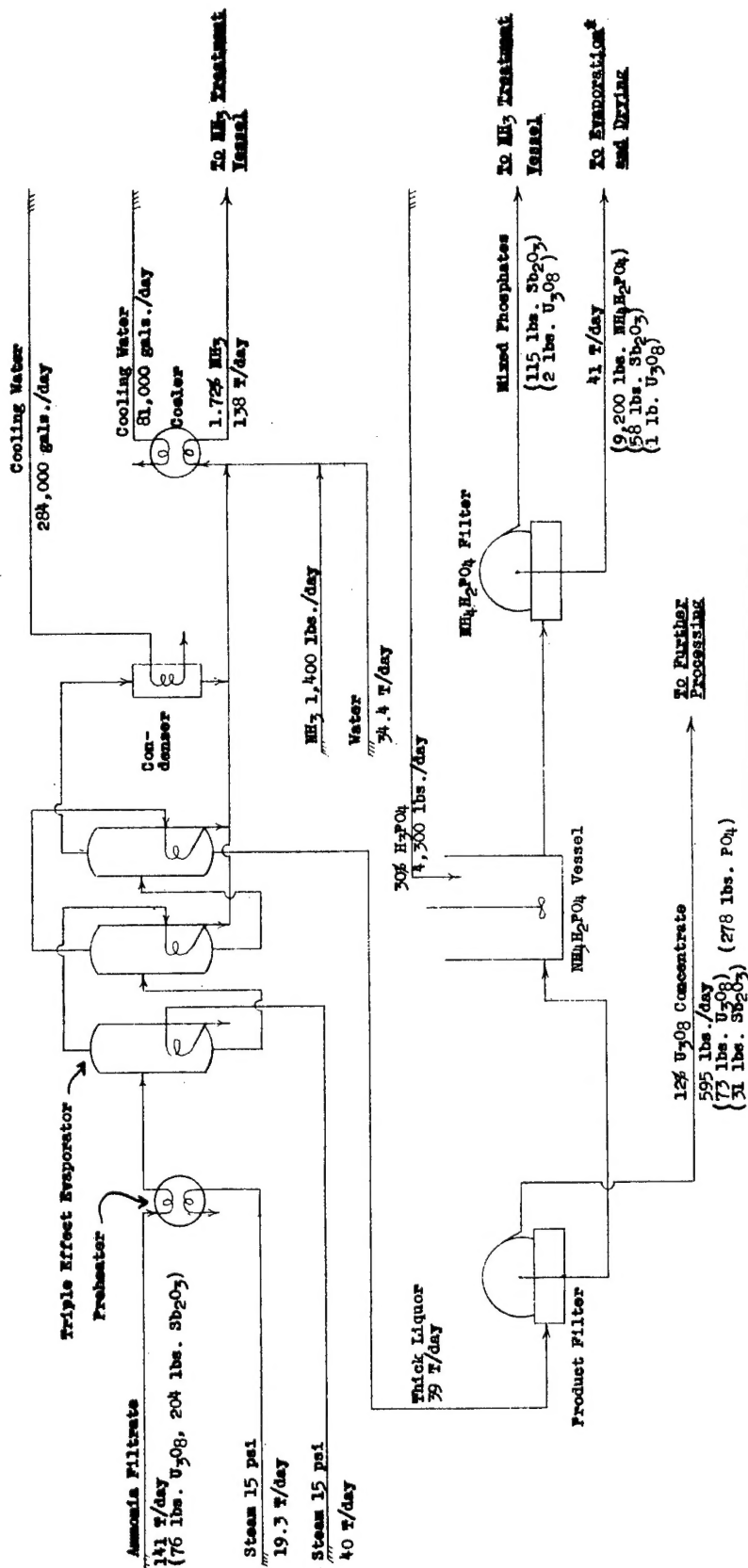
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Figure 2.

Uranium and Ammonia Recovery
Flow Sheet (Laboratory Production)

DESIGNED	DATE	SCALE
DR. H. H. H.	Jan. 10, 52	
TRACED		



* Appears in plant cost estimate as double effect evaporator and dryer. 19.7 π steam and 67 M gal. cooling water used per day.

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Uranium and Ammonium Phosphate Recovery
Flow Sheet ($NH_4H_2PO_4$ Production)

DATE	1/22/52
SCALE	
TRACED	

F. ACKNOWLEDGEMENT

The experimental work described in this report was performed by Eugene DeHaven.